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(54) CATALYST FOR DECOMPOSING AND REMOVING NITROGEN OXIDES AND DECOMPOSING AND REMOVING METHOD OF NITROGEN OXIDES

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a high-active catalyst capable of directly decomposing and removing the NO in a waste gas without a reducing agent by using the catalyst in which a composition of one kind metal composite oxide being a catalytic active ingredient is expressed by a specified formula and also one kind crystal structure has a SrTiO₃ perovskite structure.

SOLUTION: The catalyst capable of directly decomposing and removing the nitrogen monoxide without the reducing agent is produced by using the catalyst in which the composition of one kind metal composite oxide being the catalytic active ingredient of the nitrogen oxides decomposition catalyst expressed by a general formula AB_{1-x}XM_xO_{3+z}. In the formula, A is one kind metal selected from alkaline earth element, B is one kind metal selected from titanium group element, M is one kind metal selected from iron group, platinum group or copper group element, 0<x<1, (z) is an oxygen defect number or oxygen excess number of the metal oxide at normal temp. and atmospheric pressure. The metal composite oxide having the SrTiO₃ perovskite type crystal structure is used as one kind among metal composite oxide being the catalytic active principle.

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CLAIMS

[Claim(s)]

[Claim 1] Among the metal multiple oxides which are the active ingredients of a nitrogen-oxides decomposition catalyst, at least one kind of presentation general formula $AB_{1-x}M_xO_{3+z}$ (however, one kind of metal with which A was chosen from the alkaline earth element --) It is the decomposition catalyst characterized by expressing with the number of oxygen defects or the number of hyperoxia of a metallic oxide at the time of ordinary temperature atmospheric pressure one kind of metal with which one kind of metal with which B was chosen from the titanium group element, and M were chosen from iron-group, a platinum group, or copper family elements, $0 < x < 1$, and z.

[Claim 2] At least one kind in the metal multiple oxide which is a catalytic activity component is $SrTiO_3$. Decomposition catalyst according to claim 1 characterized by having the perovskite mold crystal structure.

[Claim 3] The decomposition catalyst according to claim 1 or 2 to which A in said general formula is Sr, B is Ti, and at least one kind in the metal multiple oxide which is a catalytic activity component is characterized by having the presentation as which M is expressed in Fe or Co.

[Claim 4] The decomposition catalyst according to claim 3 to which at least one kind in the metal multiple oxide which is a catalytic activity component is characterized by having the presentation expressed with $SrTi_{1-x}Fe_xO_3$ (however, $x < 1$).

[Claim 5] The decomposition catalyst according to claim 3 to which at least one kind in the metal multiple oxide which is a catalytic activity component is characterized by having the presentation expressed with $SrTi_{1-x}Co_xO_3$ (however, $x < 1$).

[Claim 6] The decomposition catalyst according to claim 1 or 2 to which A in said general formula is Sr, B is Zr, and at least one kind in the metal multiple oxide which is a catalytic activity component is characterized by having the presentation as which M is expressed in Fe or Co.

[Claim 7] The decomposition catalyst according to claim 6 to which at least one kind in the metal multiple oxide which is a catalytic activity component is characterized by having the presentation expressed with $SrZr_{1-x}Fe_xO_3$ (however, $x < 1$).

[Claim 8] The decomposition catalyst according to claim 6 to which at least one kind in the metal multiple oxide which is a catalytic activity component is characterized by having the presentation expressed with $SrZr_{1-x}Co_xO_3$ (however, $x < 1$).

[Claim 9] The manufacture approach of claims 1, 2, 3, 4, 5, 6, and 7 characterized for the water solution of Sr and Ti, Zr or Hf, and each water-soluble salts of one kind of other transition metals by independent or mixing, pyrolyzing in a misty condition and calcinating the obtained powder at temperature -1000 degree C of 600 degrees C, or a nitrogen-oxides decomposition catalyst given in eight.

[Claim 10] The removal approach by direct disassembly of the nitrogen oxides characterized by contacting nitrogen oxides under the nonexistence of a reducing agent in temperature -900 degree C of 500 degrees C under the nonexistence of a decomposition catalyst according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 and oxygen.

[Claim 11] The direct decomposition removal approach of the nitrogen oxides characterized by contacting nitrogen oxides in a decomposition catalyst according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, and temperature -900 degree C of 500 degrees C under existence of oxygen.

[Claim 12] The direct decomposition removal approach of nitrogen oxides according to claim 10 or 11 that nitrogen oxides are NO.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the decomposition removal approach of nitrogen oxides of having used this for the nitrogen oxides NO_x discharged from mobile emission sources, such as a stationary source of an electric power plant etc., and a gasoline automobile, a diesel rolling stock, the catalyst which decomposes directly and removes the harmful nitrogen monoxide NO without a reducing agent epidemiologically especially, and its manufacture approach list. Incidentally, Field of application of this invention does not stop at the stack gas denitration of a combustion gas, but includes all decomposition removal of NO generated by combustion, such as air cleaning the inside of the indoor environment at the time of use of an open sand mold combustor etc., and a tunnel, or for environmental manipulation, such as an outdoor environment of the city section. Furthermore, decomposition removal of NO under exhaust air discharged by carrying out a byproduction in the manufacture process of a chemistry article is also included.

[0002]

[Description of the Prior Art] It is [the approach of carrying out reduction removal of the NO at the removal technique of nitrogen oxides, using ammonia and hydrocarbons as a reducing agent, and] direct N₂ about NO under reducing-agent nonexistence. O₂ There is the direct decomposition approach to decompose. As a former example of representation, there is an ammonia selective contact reduction method (SCR), and smoke eliminating of a works boiler etc. is NO_x in a stationary source. Although put in practical use by removal, as the denitrification approach in mobile emission sources, it is not practical.

[0003] Moreover, it is thought that it is the reduction removal method to which the three way component catalyst method (TWC) for removing three components of NO_x in exhaust gas, CO, and unburnt hydrocarbon to coincidence also uses CO and a hydrocarbon as a reducing agent by SUTOIKI combustion which burns while keeping the optimal air-fuel ratio (weight ratio of air and a fuel). By this approach, by using a Rh-Pt system catalyst, the high rate of denitrification is obtained and it is applied to the large range including mobile emission sources. However, the SUTOIKI combustion method is disadvantageous in respect of efficient and energy-saving nature.

[0004] The lean combustion with a large air-fuel ratio is a lot of O₂ in exhaust gas, although it is advantageous in respect of efficient and energy-saving nature compared with SUTOIKI combustion. Since it lives together, a Rh-Pt system three way component catalyst does not show the denitrification engine performance. NO_x under oxygen coexistence About reduction removal, although there was nothing in addition to the approach of using ammonia as a reducing agent conventionally, the reduction denitrogenizing method by the hydrocarbon is beginning to be put in practical use despite the low rate of denitrification in recent years. However, since the denitrification engine performance changes with the presentations (NO_x concentration, an oxygen density, the amount of reducing agents, in addition to this) of exhaust gas a lot, these reduction denitrogenizing methods need the facility for controlling addition and the combustion condition of a reducing agent, in order to obtain the practical rate of denitrification.

[0005] It compares with the reduction denitrogenizing method and is NO_x in exhaust gas. Direct N₂ O₂ Since the denitrification engine performance is not dependent on an exhaust gas presentation, the direct part solution method to decompose has unnecessary addition of a reducing agent, and can build an easy denitrification system. Therefore, the class of combustor is not restricted to a specific thing, either, but is wide. [of applicability] However, NO_x under an oxygen existence [like purification of the lean combustion gasoline engine exhaust gas with which 10 capacity % extent also remains, or diesel-power-plant exhaust gas] whose oxygen is Decomposition is very difficult. Although the metal support zeolite (for example, JP,60-12909,B) which added copper, Ga, Ce, etc. to ZSM-5 zeolite is proposed on laboratory level as a direct decomposition catalyst of high activity under oxygen nonexistence, this is also remarkable under oxygen existence and activity falls.

[0006] The perovskite mold metallic oxide is proposed about the direct part solution method (the Teraoka ****, Shuichi Kagawa et al., catalyst 33 (2) 73-76 (1991)), and this excels [elevated temperature / 600 degrees C or more] in activity and endurance, and it is known that the activity per catalyst unit weight is high. Especially, a presentation is $\text{La}_{0.8} \text{Sr}_{0.2} \text{CoO}_3$. It is known that the perovskite mold oxide shown has the activity per highest unit weight.

[0007] Moreover, $\text{K}_2 \text{NiF}_4 \text{La}_{1.6} \text{Sr}_{0.4} \text{CuO}_4$ which has the mold crystal structure It is known that the decomposition activity per unit surface area is the highest (Hiroyuki Yasuda, the Misonou sincerity, catalyst 33 (2) 69-72 (1991)).

[0008] However, the catalytic activity of the perovskite mold oxide known conventionally has not yet reached practical use level. although service conditions differ, if they are seen from the field of an elimination factor -- NO_x with in general satisfactory SCR method of works offgas treatment and three way component catalyst of gasoline automobile exhaust purification $\text{La}_{0.8} \text{Sr}_{0.2} \text{CoO}_3$ which is a perovskite mold oxide about direct decomposition of NO under the oxygen existence desired to an elimination factor being shown now the bottom of content oxygen 5 capacity % -- the reaction temperature of 800 degrees C -- at most -- about 10% of invert ratios is shown -- it is not alike too much.

[0009] [Problem(s) to be Solved by the Invention] target exhaust gas [this invention] -- generating from a stationary source -- be -- or generating from mobile emission sources -- be -- moreover, the fuel origin -- be -- or the combustion-air origin -- be -- let it be a technical problem to offer NO_x in the exhaust gas of all burning appliances, and the practical catalyst of high activity which decomposes directly and can remove especially NO without a reducing agent. Moreover, this invention offers a technical problem the practical manufacture approach of this high activity catalyst, and the practical exhaust gas denitrification approach of using this catalyst for a list.

[0010] [Means for Solving the Problem] According to this invention, it excels in elevated-temperature endurance and the above-mentioned technical problem is solved using a perovskite system multiple oxide with the high activity per catalyst unit weight. This invention among the metal multiple oxides which are the catalytic activity components of nitrogen-oxides decomposition namely, at least one kind of presentation general formula $\text{AB}_{1-x} \text{M}_x \text{O}_{3-z}$ (however, one kind of metal with which A was chosen from the alkaline earth element --) It is invention of the decomposition catalyst characterized by expressing with the number of oxygen defects or the number of hyperoxia of a metallic oxide at the time of ordinary temperature atmospheric pressure one kind of metal with which B was chosen from the titanium group element, one kind of metal with which M was chosen from iron-group, a platinum group, or copper family elements, $0 < x < 1$, and z.

[0011] Moreover, for this invention, at least one kind of crystal structure is SrTiO_3 among the above-mentioned metal multiple oxides preferably while at least one kind of presentation is expressed with the above-mentioned general formula among the metal multiple oxides which are catalytic activity components. It is invention of the decomposition catalyst characterized by having a perovskite mold crystal structure.

[0012] The 2nd this invention is invention of the manufacture approach of the nitrogen-oxides decomposition catalyst characterized by being independent, or mixing the water solution of Sr and Ti, Zr or Hf and iron-group [that are one kind of other transition elements], a platinum group, or each water-soluble salts of copper group metals, pyrolyzing in a misty condition, and calcinating the obtained powder in 600 degrees-C -1000 degree C of temperature requirements.

[0013] Furthermore, the 3rd this invention is invention of the removal approach by direct disassembly of the nitrogen oxides characterized by contacting nitrogen oxides for the above-mentioned decomposition catalyst under existence of oxygen or nonexistence under the nonexistence of a reducing agent at 500 degrees-C -900 degree C of temperature requirements.

[0014] In this invention, A in a general formula is in any of one kind of metal chosen from the alkaline earth element, i.e., calcium, Sr, or Ba, and calcium or its Sr is desirable on practical use. The metal belonging to an alkaline earth element has the ionic radius which is easy to produce such structure from relation with the perovskite mold crystal structure indicated below, and is desirable.

[0015] In this invention, B in a general formula is one kind of metal chosen from the titanium group element, i.e., any one kind of transition metals of Ti, Zr, or Hf. Moreover, in this invention, M in a general formula is any one kind of metal chosen from iron-group, i.e., Fe, Co, or nickel, a platinum group, i.e., Ru, Rh, Pd, Os, Ir, or Pt, or copper group, i.e., Cu, Ag, or Au.

[0016] although M has the relation which permutes a part of B in a crystal lattice here -- M or B -- either (namely, $x = 0$ or 1) -- **** -- as shown in the example of a comparison, sufficient denitrification engine performance is not obtained, but it is required for both presentations of the decomposition catalyst of this

invention for M and B to exist. Practically, the 8th group of the periodic table or 1B group element is desirable as M. The iron-group metal of Fe, nickel, and Co is excellent in the denitrification engine performance, and especially desirable. In addition, since it depends on the permutation relation between B and M, fluctuation is produced in the number of the oxygen in said general formula and a deficit or an excess is produced focusing on a basic number 3, this is expressed with $3+z$.

[0017] Moreover, the perovskite type structure in this invention is the chemical formula ABX_3 represented with perovskite (perovskite and $CaTiO_3$) as a fundamental crystal structure. One format of the crystal structure belonging to the cubic system which a compound has is meant. However, the crystal structure which distortion of some has produced is also included in a crystal lattice by the metal atomic radius which permutes a part or all of calcium or Ti in this invention, respectively, and it is $SrTiO_3$. The above-mentioned name is used as a comprehensive name of mold structure.

[0018] Generally NO is N_2 directly. O_2 which the catalyst front face generated by decomposition when decomposing O_2 in exhaust gas Although there is an inclination covered, since a perovskite mold oxide causes balking of adsorption oxygen easily, such covering cannot take place comparatively easily.

[0019] Moreover, in a perovskite system multiple oxide, the oxidation reduction reaction (redox reaction) to which the oxidation number of the transition metals to contain is changed tends to occur, and perovskite acts so that an oxidation reduction reaction may advance quickly and regularly.

[0020]

[Embodiment of the Invention] The nitrogen-oxides decomposition catalyst of this invention among the metal multiple oxides which are active ingredients at least one kind of presentation General formula $AB_{1-x}M_xO_{3+z}$ It is the decomposition catalyst which contains the transition-metals multiple oxide of the presentation expressed as an active ingredient. Especially, A is Sr, B is Ti or Zr, and it is general formula $SrTi_{1-x}M_xO_3$. Or especially the decomposition catalyst that makes an active ingredient the transition-metals multiple oxide of the presentation expressed with $SrZr_{1-x}M_xO_3$ (M shows Fe or Co in both general formulas) is desirable.

[0021] While a presentation is expressed with general formula $AB_{1-x}M_xO_{3+z}$, as for at least one kind in the metal multiple oxide whose nitrogen-oxides decomposition catalyst of this invention is a catalytic activity component, a crystal structure has the perovskite type structure of comprehensive semantics as mentioned above preferably. Catalytic activity [what became perovskite type structure among the metallic oxides of the actually studied various presentations] was high. Especially, especially the single phase perovskite that consists of only perovskite phases has high activity. Although that in which the peak which the peak of perovskite exists in the peak of an X diffraction at least, and originates in oxide other than this with this is intermingled also has activity, activity is lower than single phase perovskite generally. However, if a presentation is not a multiple oxide applicable to said general formula as the example of a comparison showed later, even if only a crystal structure has perovskite type structure, the technical problem of this invention will not be attained.

[0022] $SrTiO_3$ from which the inside B of a general formula is equivalent to $x=1$ in a known multiple oxide with Ti, and $SrFeO_3$ whose M is iron in $x=0$ Having both perovskite type structures is known and the multiple oxide by which a presentation is expressed with the above-mentioned general formula can take perovskite type structure by controlling the manufacture conditions of baking and others.

[0023] the decomposition catalyst of this invention -- warming of water-soluble metal salts, such as a nitrate, -- it can manufacture by pyrolyzing and calcinating the obtained powder in 600-degree-C elevated temperature of -1000 degree C by making a water solution into the Myst condition by using a rotary atomizer (rotary atomizer) etc., for example, passing heating space, such as an electric furnace. By this approach, a catalyst is acquired as powder of the calcinated multiple oxide.

[0024] Above-mentioned Myst may make Myst the predetermined water solution which boiled comparatively and was mixed beforehand using a spray dryer in the range in which the spray of the water solution which contains one kind of water-soluble metal salt, respectively may be carried out to coincidence, and it may be generated, and salts do not generate precipitate.

[0025] In order that oxide may take perovskite type structure, 600 degrees C or more of burning temperature are desirable. Moreover, as for burning temperature, it is desirable that it is temperature higher than service temperature in order to hold the stability at the time of use of a catalyst, and endurance. However, since service temperature continues broadly according to the condition of target exhaust gas, the burning temperature of a catalyst cannot generally be limited.

[0026] In addition, if it is beyond the predetermined temperature from which burning temperature produces perovskite type structure, it is rare for perovskite type structure to change, but since the transition metals which exist in the crystal defect inside a crystal during baking move to a front face by solid phase diffusion etc., the presentation on the front face of a catalyst changes delicately. Therefore, when activity may change with burning temperature and it exceeds 1000 degrees C, activity is difficult to get in a high thing generally. If in

charge of operation, according to the condition of object exhaust gas, it is necessary to choose the optimal burning temperature experimentally.

[0027] Thus, the catalyst of obtained this invention has a specific surface area as large as 7-10m² / g measured with the BET adsorption method. others -- Fe 2O₃, SrO₂, and TiO₂ etc. -- although there was a solid phase technique which mixes a solid acid ghost and is calcinated at about 1000 degrees C, the specific surface area of the catalyst acquired was under 1m² / g. Moreover, in the solution method which mixes the water solution of a metal salt, is made to carry out coprecipitation of the precipitate of salts, and dries, or dries the mixed liquor whole quantity, makes a precursor, and calcinates solids, such as this, at 850 to 1000 degree C, the specific surface area of the catalyst acquired was 1-5m² / g. In the so-called water-solution spray method of this invention, a big specific surface area has been obtained by adding organic acids, such as a suitable urea making the decomposition reaction of a metal salt perfect, sucrose, or a malic acid, as an additive.

[0028] Although it may be used for it with shaping assistants, such as a binder remaining as it is or suitable, at a pellet type, carrying out extrusion molding of the catalytic activity component manufactured as mentioned above to the shape of extrusion, compression molding, or a honeycomb etc., you may use it, making the support of this business world common knowledge support suitably.

[0029] Without adding reducing agents, such as ammonia and a hydrocarbon, to exhaust gas using the decomposition catalyst of this invention, a catalyst can be made to be able to contact and nitrogen oxides can be understood by direct. There is a limitation in applying the reduction catalyst which needs a reducing agent to the nitrogen-oxides decomposition removal in the exhaust gas from mobile emission sources or a small stationary source, and direct decomposition is one of the big advantages of this invention.

[0030] The catalyst of fixed-bed circulation mold reactors, such as a well-known packed bed type or a plate type, or this invention can utilize an advantage with the high activity per unit weight, and can perform contact to a decomposition catalyst and exhaust gas in this industry with a fluid bed mold reactor. Moreover, various practical gestalten can be taken according to the class and scale of the source of discharge, and this invention is not limited to this.

[0031] The temperature which contacts exhaust gas for a decomposition catalyst has desirable 500-degree-C-900 degree C with the high decomposition activity of the catalyst of this invention. The operating temperature of denitrification processing of nitrogen oxides according to the catalyst of this invention to offgas treatment of 300 to 400 degree C, a gasoline engine, or a gas turbine being performed at 400 to 450 degree C has the unnecessary temperature control which the special feature is in the point that the works offgas treatment according to 200 degrees C or less and a vanadium titanium system catalyst in other denitrification processings, for example, the offgas treatment of a city incinerator, is an elevated temperature, and lowers exhaust gas temperature beforehand using a cooling means etc.

[0032]

[Example] Although an example is indicated in order to explain this invention still more concretely, thereby, this invention is not limited. In addition, all %s that show a gas presentation here are capacity %s, and all %s that show the presentation of a catalyst and a raw material, and intermediate field are weight %s. Moreover, the decomposition activity of a catalyst is N₂ of NO. It expresses with an invert ratio and calculates with a formula 1.

[0033]

[Formula 1] cracking severity = -- 2[N₂] out / [NO] in -- here -- [N₂] out N₂ of reactor outlet gas Concentration [NO] in NO concentration [0034] of reactor inlet-port gas [Example 1]

example of preparation 1Fe(NO₃)₂ and 6H₂O of a catalyst, and Ti (NO₃)₄ and every of Sr(NO₃)₂ and 2H₂O -- by equivalent ratio, 0.4:0.6:1 came out comparatively, 0.4M water solution was prepared, the additive was added, and it mixed at the room temperature. The rotary atomizer was supplied warming this at 350 degrees C, the spray was adiabatically carried out into airstream at 120 degrees C from the nozzle which adjusted the amount of spraying to a part for 100cm³/, the inside of the electric furnace held at 350 degrees C in the state of fog was dropped, uptake was carried out with the cyclone which prepared the generated fine particles in the lower part of a furnace, and raw material powder was obtained. Temporary quenching of this raw material powder is carried out at 650 degrees C in air for 1 hour, and, subsequently it calcinates at 850 degrees C for 5 hours, and is catalytic activity component SrTi_{0.6} Fe 0.4O₃. Powder was obtained. By the X-ray crystallographic analysis of this thing, it checked that this catalyst component had the perovskite mold crystal structure. It is this powder 500 kgf/cm³ It is compressive force, isotropic pressure shaping was carried out, the obtained pellet was ground and classified, and catalyst SrTi_{0.6} Fe 0.4O₃ of granularity this invention whose grain size is 0.31mm - 0.71 mm was obtained. Specific surface area is N₂ in the liquid nitrogen temperature of this granulation. It measured with the BET adsorption method from the amount of adsorption, and they were 7.4m² / g.

[0035] The catalyst of this invention to which equivalent ratio is changed and a Ti/Fe ratio corresponds to

0.8/0.2 from 0.2/0.8 was acquired using the example of preparation 2 above-mentioned raw material of a catalyst.

[0036] Filling up a cylindrical shape packed bed mold reactor with evaluation 1 bore [of decomposition activity] of 10mm with the 5.0g of the above-mentioned catalysts, carrying out electric heat heating of the reactor outer wall, and maintaining the temperature of a catalyst bed at predetermined It is 1%NO content helium gas (namely, under oxygen nonexistence) Contact time $W/F=3.0 \text{ g-sec/cm}^3$ By the becoming flow rate (a part for namely, $100\text{cm}^3/\text{s}$), sink, N_2 of outlet gas Concentration is measured with a gas-chromatograph analyzer and it is N_2 from NO by the formula 1. It calculated as an invert ratio and was shown in Table 1. In addition, W/F has the dimension of the contact time which displays the catalytic activity per catalyst unit weight, and is calculated by the formula 2.

[0037]

[Formula 2]

The $W/F = \text{catalyst (weight g)} / \text{reactor inflow gas flow rate (cm}^3 / \text{sec)}$

$= [\text{g}][\text{sec}] / [\text{cm}^3]$

[0038] $\text{SrTi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ of evaluation 2 this invention of decomposition activity NO is 1% and O_2 like [a catalyst] the above-mentioned evaluation 1. 10%, helium contacted 89% of mixed gas (namely, under oxygen coexistence), investigated decomposition activity, and showed the result in Table 1.

[0039] As Table 1, NO invert ratio of the decomposition catalyst of this invention is notably higher than a known perovskite mold catalyst, and the inclination which activity moreover increases with temperature to 90% or more of invert ratios also in the decomposition temperature of 800 degrees C or more hears from the evaluation result in the above mentioned reaction temperature of 600,700,800 degrees C about it. Moreover, it turns out that the decomposition catalyst of this invention has high decomposition activity also under existence of oxygen.

[0040] [Example 2]

It replaces with the first ferrum water solution of example of preparation 3 nitric acid of a catalyst, and is Co (NO_3)₂. 0.4M water solution was used, and also it is catalyst $\text{SrTi}_{0.6}\text{Co}_{0.4}\text{O}_3$ of this invention like the above-mentioned example 1 of preparation. It obtained.

[0041] The catalyst of this invention to which equivalent ratio is changed and a Ti/Co ratio corresponds to 0.9/0.1 from 0.2/0.8 was acquired using the example of preparation 4 above-mentioned raw material of a catalyst.

[0042] Like the evaluation 1 above of decomposition activity, activity evaluation in the reaction temperature of 600,700,800 degrees C was performed using NO content helium gas (namely, oxygen nonexistence) 1%, and the result was shown in Table 1. The decomposition catalyst of this invention has activity higher than a known perovskite mold multiple oxide, and, moreover, is understood that activity is more large in an elevated-temperature field.

[0043] [Example 3]

example of preparation $5\text{Fe}(\text{NO}_3)_2$ and $6\text{H}_2\text{O}$ of a catalyst, and $\text{Zr}(\text{NO}_3)_4$ and $5\text{H}_2\text{O}$ and every of $\text{Sr}(\text{NO}_3)_2$ and $2\text{H}_2\text{O}$ -- and also it used 0.4M water solution -- the example 1 of preparation of said example 1 -- the same -- carrying out -- catalyst $\text{SrZr}_{0.8}\text{Fe}_{0.2}\text{O}_3$ of this invention It obtained.

[0044] Like the evaluation 1 above of decomposition activity, activity evaluation was performed using NO content helium gas (namely, oxygen nonexistence) 1%, and the result was shown in Table 1. The decomposition catalyst of this invention has activity higher than a known perovskite mold multiple oxide, and is understood that activity is more large in an elevated-temperature field.

[0045] [Example 4]

It replaces with the first ferrum water solution of example of preparation 6 nitric acid of a catalyst, and is Co (NO_3)₂. 0.4M water solution was used, and also it is catalyst $\text{SrZr}_{0.8}\text{Co}_{0.2}\text{O}_3$ of this invention like the above-mentioned example 5 of preparation. It obtained.

[0046] Like the evaluation 1 above of decomposition activity, activity evaluation was performed using NO content helium gas (namely, oxygen nonexistence) 1%, and the result was shown in Table 1. The decomposition catalyst of this invention has activity higher than a known perovskite mold multiple oxide, and is understood that activity is more large in an elevated-temperature field.

[0047] General formula $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ of [example 1 of comparison] this invention The perovskite mold multiple oxide SrFeO_3 equivalent to $x=1$ and $x=0$, and SrTiO_3 It prepared like the example 1, respectively, activity evaluation was performed like the example 1, and the result was shown in Table 1. It turns out that decomposition activity does not reach distantly [catalyst / of this invention / decomposition].

[0048] General formula $\text{SrTi}_{1-x}\text{Co}_x\text{O}_3$ of [example 2 of comparison] this invention Perovskite mold multiple oxide SrCoO_3 equivalent to $x=1$ It prepared like the example 2, activity evaluation was performed like the example 2, and the result was shown in Table 1. It turns out that decomposition activity does not attain to the

decomposition catalyst of this invention far.

[0049] General formula $\text{SrZr}_{1-x}\text{M}_x\text{O}_3$ of [example 3 of comparison] this invention Perovskite mold multiple oxide SrZrO_3 equivalent to $x=0$ It prepared like the example 3, activity evaluation was performed to said this appearance, and the result was shown in Table 1. It turns out that decomposition activity is less than NO decomposition catalyst of this invention.

[0050] It is $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ which has specific surface area of $4.9\text{m}^2/\text{g}$ which manufactured like the example 1 and was obtained and which is a known perovskite mold metallic oxide except having used the water solution of a [example 4 of comparison] La nitrate, Sr nitrate, and Co nitrate. It used, the same reactor as an example 1 was used, and the result evaluated by the same conditions was indicated to Table 1. Although activity is quite high compared with the multiple oxide of the above-mentioned example 1 of a comparison, as compared with the decomposition catalyst of this invention, the activity in 700 degrees C and 800 degrees C is about 60 percent, and it is shown that the increment in activity is seldom expectable even if it raises temperature to 800 degrees C or more, and it turns out that both B and M in said general formula are need. Moreover, compared with the decomposition catalyst of this invention, it turns out that the activity fall under oxygen existence is also intense.

[0051]

[Table 1]

		The oxygen in exhaust gas		Oxygen nonexistence	Oxygen coexistence
O ₂ =0% O ₂ =10%				reaction temperature	** 600 700 800 800
example 1		SrTi _{0.2} Fe 0.8O ₃	5.1 11.1 14.6	SrTi _{0.4} Fe 0.6O ₃	11.8 40.8 67.9
Fe _{0.4} O ₃	13.8 51.4 79.1 46.1	SrTi _{0.8} Fe 0.2O ₃	13.5 52.8 82.7	Example 2	SrTi _{0.2} Co 0.8O ₃ 5.5 15.2 25.9
Co 0.4O ₃	10.0 33.3 52.0	SrTi _{0.8} Co _{0.2} O ₃	13.8 51.4 79.1	SrTi _{0.9} Co 0.1O ₃	13.5 51.6 79.6
Example 3	SrZr _{0.8} Fe 0.2O ₃	13.2 48.3 72.4	Example 4	SrZr _{0.8} Co 0.2O ₃	10.1 30.1 45.6
Example 1 of a comparison	SrFeO ₃	2.1 6.3 7.5	SrTiO ₃	2.7 10.6 22.9	Example of comparison 2
SrCoO ₃	2.8 14.4 14.0	Example of comparison 3	SrZrO ₃	2.212.9	40.0
Example 4 of a comparison	La _{0.8} Sr _{0.2} CoO ₃	9.2 26.1 42.0	8.4		

[0052]

[Effect of the Invention] The nitrogen-oxides decomposition catalyst of this invention is direct N₂ at high cracking severity about NO, without using a reducing agent. O₂ Since it can decompose, the denitrification engine performance is not dependent on the presentation of exhaust gas, or the class of combustor, and broad application is possible. Moreover, equipment of the running cost of reducing-agent use, a reducing-agent supply control unit, etc. is unnecessary, and, also economically, it excels.

[0053] The nitrogen-oxides decomposition catalyst of this invention is [0054] suitable for direct decomposition removal of NO discharged also under oxygen existence from a diesel power plant with the comparatively loose fall of activity, and the high air-fuel ratio which contains remarkable oxygen in exhaust gas etc. The nitrogen-oxides decomposition catalyst of this invention is conventional NO_x. Since the inclination for the temperature which decomposition activity discovers compared with a decomposition catalyst to follow on becoming [in / moreover / it is high and / a certain temperature requirement] an elevated temperature at 600 degrees C or more, and for activity to also become high is strong, it is NO_x in elevated-temperature exhaust gas. It is suitable for decomposition removal.

[0055] In case the decomposition catalyst of this invention is used, in order not to reduce exhaust gas temperature with means, such as cooling, like the conventional catalyst, offgas treatment equipment is made into a compact and the applicability to home use or an indoor air defecation application is large.

[Translation done.]

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最終頁に続く

(54) 【発明の名称】 窒素酸化物の分解除去用触媒及び窒素酸化物の分解除去方法

(57) 【要約】

【課題】 固定発生源であれ或は移動発生源であれ、また燃料由来であれ或は燃焼空気由来であれ、全ての燃焼機器の排ガス中のNO_x。就中NOを還元剤無しに高温で直接分解し除去する実用的な高活性分解触媒、この高活性触媒の実用的な製造方法、並びにこの触媒を用いる実用的な排ガス脱硝方法を提供する。

【解決手段】 組成が一般式A B_{1-x} M_x O_{3-2x} (Aはアルカリ土類金属、Bはチタン族、Mは鉄族、白金族又は銅族金属から選ばれた各1種類) で表され、好ましくは結晶構造がペロブスカイト型である金属複合酸化物を少なくとも1種類触媒活性成分として含む窒素酸化物分解触媒を用いる。この触媒は水溶性金属塩類の水溶液をスプレー法により霧状で熱分解して得た粉末を仮焼し、高温で焼成して製造する。この触媒に窒素酸化物を還元剤の非存在下で、酸素共存または非存在下で600℃-1000℃で接触させる。

【特許請求の範囲】

【請求項1】 窒素酸化物分解触媒の活性成分である金属複合酸化物のうち少なくとも1種類の組成が、一般式 $AB_{1-x}M_zO_{3-x}$ (但しAはアルカリ土類元素から選ばれた1種類の金属、Bはチタン族元素から選ばれた1種類の金属、Mは鉄族、白金族または銅族元素から選ばれた1種類の金属、 $0 < x < 1$ 、zは常温大気圧時における金属酸化物の酸素欠陥数或は酸素過剰数)で表されることを特徴とする分解触媒。

【請求項2】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、 $SrTiO_3$ 、ペロブスカイト型結晶構造を有することを特徴とする請求項1記載の分解触媒。

【請求項3】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、前記一般式におけるAがSrであり、BがTiであり、MがFeまたはCoで表される組成を有することを特徴とする請求項1または2記載の分解触媒。

【請求項4】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、 $SrTi_{1-x}Fe_xO_3$ (但しxは $0 < x < 1$)で表される組成を有することを特徴とする請求項3記載の分解触媒。

【請求項5】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、 $SrTi_{1-x}Co_xO_3$ (但しxは $0 < x < 1$)で表される組成を有することを特徴とする請求項3記載の分解触媒。

【請求項6】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、前記一般式におけるAがSrであり、BがZrであり、MがFeまたはCoで表される組成を有することを特徴とする請求項1または2記載の分解触媒。

【請求項7】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、 $SrZr_{1-x}Fe_xO_3$ (但しxは $0 < x < 1$)で表される組成を有することを特徴とする請求項6記載の分解触媒。

【請求項8】 触媒活性成分である金属複合酸化物のうち少なくとも1種類が、 $SrZr_{1-x}Co_xO_3$ (但しxは $0 < x < 1$)で表される組成を有することを特徴とする請求項6記載の分解触媒。

【請求項9】 Sr、及びTi又はZr若しくはHf、及び他の1種類の遷移金属の各水溶性塩類の水溶液を単独または混合して、霧状態において熱分解し、得られた粉末を温度 600°C — 1000°C で焼成することを特徴とする請求項1、2、3、4、5、6、7または8記載の窒素酸化物分解触媒の製造方法。

【請求項10】 窒素酸化物を還元剤の非存在下で、温度 500°C — 900°C において請求項1、2、3、4、5、6、7、8または9記載の分解触媒と酸素の非存在下で接触させることを特徴とする窒素酸化物の直接分解による除去方法。

【請求項11】 窒素酸化物を酸素の存在下で請求項1、2、3、4、5、6、7、8または9記載の分解触媒と温度 500°C — 900°C において接触させることを特徴とする窒素酸化物の直接分解除去方法。

【請求項12】 窒素酸化物がNOである請求項10または11記載の窒素酸化物の直接分解除去方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、発電所等の固定発生源やガソリン自動車、ディーゼル車等の移動発生源から排出される窒素酸化物NO_x、特に、疫学的に有害な一酸化窒素NOを還元剤なしに直接分解して除去する触媒、その製造方法並びにこれを用いた窒素酸化物の分解除去方法に関する。因みに、本発明の適用分野は燃焼排ガスの排煙脱硝に止まらず、開放型燃焼器等の使用時の室内環境、トンネル内或は都市部の屋外環境等の環境改善のための空気清浄化など、燃焼により生成した全てのNOの分解除去を包含する。更には、化学品の製造プロセスにおいて副生し排出される排気中のNOの分解除去をも包含する。

【0002】

【従来の技術】窒素酸化物の除去技術には、アンモニア、炭化水素類等を還元剤として用いてNOを還元除去する方法と、還元剤非存在下でNOを直接N₂とO₂とに分解する直接分解方法がある。前者の代表例としてはアンモニア選択的接触還元法(SCR)があり、工場ボイラーの排煙等固定発生源でのNO_x除去に実用化されているが、移動発生源での脱硝方法としては実用的ではない。

【0003】また、空燃比(空気と燃料の重量比)を最適に保ちながら燃焼するストイキ燃焼により、排ガス中のNO_x、CO、未燃炭化水素類の3成分を同時に除去する三元触媒法(TWC)も、COや炭化水素を還元剤とする還元除去法であると考えられる。この方法ではRh-Pt系触媒を用いることにより高い脱硝率が得られており、移動発生源を含めた広い範囲に適用されている。しかし、ストイキ燃焼方法は高効率、省エネルギー性の点で不利である。

【0004】空燃比の大きい希薄燃焼は、ストイキ燃焼に比べ高効率、省エネルギー性の面で有利であるが、排ガス中に大量のO₂が共存するためRh-Pt系三元触媒は脱硝性能を示さない。酸素共存下におけるNO_xの還元除去については、従来アンモニアを還元剤として用いる方法以外に無かったが、近年炭化水素による還元脱硝法が、低い脱硝率ながらも実用化されはじめている。しかしながら、これらの還元脱硝法は排ガスの組成(N₂O₂濃度、酸素濃度、還元剤量、その他)によって脱硝性能が大きく変化するので、実用的な脱硝率を得るためには還元剤の添加や燃焼状態を制御するための設備を必要とする。

【0005】還元脱硝法に比べて、排ガス中の NO_x を直接 N_2 と O_2 とに分解する直接分解法は、脱硝性能が排ガス組成に依存しないため還元剤の添加が不要で、簡単な脱硝システムを構築することが可能である。従って、燃焼器の種類も特定のものに限られず適用範囲が広い。しかし、酸素が10容量%程度も残存する希薄燃焼ガソリンエンジン排ガスやディーゼルエンジン排ガスの浄化のような酸素存在下での NO_x 分解は極めて困難である。酸素非存在下での高活性の直接分解触媒として、実験室レベルでは、ZSM-5ゼオライトに銅、Ga、Ce等を添加した金属担持ゼオライト（例えば特公昭60-12909号公報）が提案されているが、これも酸素存在下では著しく活性が低下する。

【0006】直接分解法については、ペロブスカイト型金属酸化物が提案されており（寺岡靖剛、鹿川修一ら、触媒 33（2）、73-76（1991））、これは600℃以上の高温でも活性及び耐久性に優れており、また触媒単位重量当たりの活性が高いことが知られている。中でも、組成が $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ で示されるペロブスカイト型酸化物は最高の単位重量当たりの活性を有することが知られている。

【0007】また、 K 、 NiF 、型結晶構造を有する $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_3$ は、単位表面積当たりの分解活性が最高であることが知られている（安田弘之、御園生誠ら、触媒 33（2）、69-72（1991））。

【0008】しかし、従来知られているペロブスカイト型酸化物の触媒活性は、未だ実用レベルに達していない。使用条件は異なるものの除去率の面から見ると、工場排ガス処理のSCR法やガソリン自動車排ガス浄化の三元触媒が概ね満足な NO_x 除去率を示すのに対し、現在望まれている酸素存在下での NO_x の直接分解に関しては、ペロブスカイト型酸化物である $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ は含有酸素5容量%の下で反応温度800℃で高々転化率10%程度を示すに過ぎない。

【0009】

【発明が解決しようとする課題】本発明は、対象とする排ガスが固定発生源からの発生であれ或いは移動発生源からの発生であれ、また燃料由来であれ或は燃焼空気由来であれ、全ての燃焼機器の排ガス中の NO_x 、特に NO を還元剤なしに直接分解して除去できる実用的で高活性の触媒を提供することを課題とする。また本発明はこの高活性触媒の実用的な製造方法、並びにこの触媒を用いる実用的な排ガス脱硝方法の提供を課題とする。

【0010】

【課題を解決するための手段】本発明によれば、高温耐久性に優れ、触媒単位重量当たりの活性が高いペロブスカイト系複合酸化物を用いて上記課題が解決される。即ち本発明は、窒素酸化物分解の触媒活性成分である金属複合酸化物のうち少なくとも1種類の組成が、一般式A

$\text{B}_{1-x}\text{M}_x\text{O}_{3-z}$ （但しAはアルカリ土類元素から選ばれた1種類の金属、Bはチタン族元素から選ばれた1種類の金属、Mは鉄族、白金族または銅族元素から選ばれた1種類の金属、 $0 < x < 1$ 、zは常温大気圧時における金属酸化物の酸素欠陥数或は酸素過剰数）で表されることを特徴とする分解触媒の発明である。

【0011】また本発明は、触媒活性成分である金属複合酸化物のうち少なくとも1種類の組成が上記一般式で表されると共に、好ましくは上記金属複合酸化物のうち少なくとも1種類の結晶構造が SrTiO_3 、ペロブスカイト型結晶構造を有することを特徴とする分解触媒の発明である。

【0012】第2の本発明は、 Sr 、及び Ti 又は Zr 若しくは Hf 、及び他の1種類の遷移元素である鉄族、白金族または銅族金属の各水溶性塩類の水溶液を単独で、または混合して、霧状態において熱分解し、得られた粉末を温度範囲600℃-1000℃において焼成することを特徴とする窒素酸化物分解触媒の製造方法の発明である。

【0013】更に第3の本発明は、窒素酸化物を還元剤の非存在下で、酸素の存在下または非存在下において温度範囲500℃-900℃で上記の分解触媒と接触させることを特徴とする窒素酸化物の直接分解による除去方法の発明である。

【0014】本発明において、一般式中のAは、アルカリ土類元素から選ばれた1種類の金属、即ち Ca 、 Sr または Ba の何れかであり、実用上、特に Ca または Sr が好ましい。アルカリ土類元素に属する金属は、次に記載するペロブスカイト型結晶構造との関係から、このような構造を生じ易いイオン半径を有しており、好ましい。

【0015】本発明において一般式中のBは、チタン族元素から選ばれた1種類の金属、即ち Ti 、 Zr または Hf の何れか1種類の遷移金属である。また、本発明において一般式中のMは、鉄族即ち Fe 、 Co または Ni 、白金族即ち Ru 、 Rh 、 Pd 、 Os 、 Ir または Pt 、或は銅族即ち Cu 、 Ag または Au から選ばれた何れか1種類の金属である。

【0016】ここで、Mは結晶格子においてBの一部を置換する関係にあるが、MまたはB何れか一方のみ（即ち $x=0$ または 1 ）では、比較例に示したように充分な脱硝性能が得られず、本発明の分解触媒の組成にはM及びBが共に存在することが必要である。実用上、Mとして周期律表第8族または1B族元素が好ましい。特に Fe 、 Ni 、 Co の鉄族金属が脱硝性能に優れており、好ましい。なお、BとMの置換関係に依り、前記一般式中の酸素の数に変動を生じ、基本数3を中心として欠損または過剰を生じるので、これを $\pm z$ で表している。

【0017】また本発明におけるペロブスカイト型構造は、基本的な結晶構造としては灰チタン石（perov

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skite, CaTiO_3) で代表される化学式 ABX , の化合物が有する立方晶系に属する結晶構造の一形式を意味する。但し、本発明では夫々 Ca 、または Ti の一部または全部を置換する金属の原子半径によって結晶格子に多少の歪みが生じている結晶構造も含めて、 SrTiO_3 型構造の包括的名称として上記名称を用いる。

【0018】一般に NO が直接的に N_2 と O_2 とに分解する際に、触媒表面が分解で生成した O_2 、或いは排ガス中の O_2 、によって被覆される傾向があるが、ペロブスカイト型酸化物は容易に吸着酸素の離脱を起こすため、こ

のような被覆が比較的起こり難い。
【0019】またペロブスカイト系複合酸化物では、含有される遷移金属の酸化数が変動する酸化還元反応 (redox 反応) が起こり易く、ペロブスカイトは酸化還元反応が迅速且つ定期的に進行するように作用する。

【0020】

【発明の実施の形態】本発明の窒素酸化物分解触媒は、活性成分である金属複合酸化物のうち少なくとも1種類の組成が、一般式 $\text{AB}_{1-x}\text{M}_x\text{O}_{3-x}$ で表される組成の遷移金属複合酸化物を活性成分として含む分解触媒であり、中でも A が Sr 、 B が Ti または Zr であって、一般式 $\text{SrTi}_{1-x}\text{M}_x\text{O}_3$ 、または $\text{SrZr}_{1-x}\text{M}_x\text{O}_3$ 、(両一般式において M は Fe または Co を示す) で表される組成の遷移金属複合酸化物を活性成分とする分解触媒が特に好ましい。

【0021】本発明の窒素酸化物分解触媒は、触媒活性成分である金属複合酸化物のうち少なくとも1種類は、組成が一般式 $\text{AB}_{1-x}\text{M}_x\text{O}_{3-x}$ で表されると共に、好ましくは結晶構造が前記のように包括的意味のペロブスカイト型構造を有するものである。実際に研究した種々の組成の金属酸化物のうち、ペロブスカイト型構造になったものが触媒活性が高かった。中でも、ペロブスカイト相のみで構成されている単相ペロブスカイトが特に活性が高い。X線回折のピークに少なくともペロブスカイトのピークが存在しこれと共にこれ以外の酸化物に由来するピークが混在しているものも活性を有するが、概して単相ペロブスカイトより活性が低い。しかし、後に比較例で示したように、組成が前記一般式に該当する複合酸化物でなければ、結晶構造のみペロブスカイト型構造を有しても本発明の課題は達成されない。

【0022】既知の複合酸化物では、一般式中 B が Ti で $x=1$ に相当する SrTiO_3 、及び $x=0$ で M が鉄である SrFeO_3 は共にペロブスカイト型構造を持つことが知られており、組成が上記一般式で表される複合酸化物は、焼成その他の製造条件を制御することによりペロブスカイト型構造をとることができる。

【0023】本発明の分解触媒は、硝酸塩など水溶性金属塩類の加温水溶液を回転噴霧器 (ロータリー・アトマイザー) を用いる等の手法によりミスト状態とし、例えば電気炉等の加熱空間を通過させることにより熱分解

し、得られた粉末を 600°C - 1000°C の高温において焼成することにより製造することができる。この方法では、触媒は焼成された複合酸化物の粉末として得られる。

【0024】上記ミストは、それぞれ1種類の水溶性金属塩を含む水溶液を同時にスプレーして生成しても良く、また塩類が沈殿を生成しない範囲で所定の割合に予め混合した水溶液をスプレッドライヤーを用いてミストにしても良い。

【0025】焼成温度は、酸化物がペロブスカイト型構造をとるようにするため 600°C 以上が好ましい。また焼成温度は、触媒の使用時の安定性、耐久性を保持するため使用温度より高い温度であることが好ましい。しかし対象とする排ガスの状態により使用温度が広範囲に亘るので、触媒の焼成温度は一概に限定できない。

【0026】なお、焼成温度がペロブスカイト型構造を生じる所定の温度以上であればペロブスカイト型構造が変わることは少ないが、焼成中に結晶内部の結晶欠陥に存在する遷移金属が固相拡散等により表面へ移動してくるので、触媒表面の組成が微妙に変化する。従って焼成温度により活性が異なることがあり、 1000°C を超えると概して活性が高いものを得難い。実施に当たっては、対象排ガスの状態に応じて、最適な焼成温度を実験的に選択する必要がある。

【0027】このようにして得た本発明の触媒は、 BE T 法で測定した比表面積が $7-10\text{m}^2/\text{g}$ と大きい。他に、 Fe 、 O_2 、 SrO_2 、 TiO_2 等の固体酸化物を混合して 1000°C 程度で焼成する固相法があるが、得られる触媒の比表面積は $1\text{m}^2/\text{g}$ 未満であった。また金属塩の水溶液を混合し、塩類の沈殿を共沈させて乾燥し、或いは混合液全量を乾燥して前駆体を作り、これ等の固形物を $850-1000^\circ\text{C}$ で焼成する溶液法では、得られる触媒の比表面積は $1-5\text{m}^2/\text{g}$ であった。本発明の所謂水溶液スプレー法では、金属塩の分解反応を完全にするのに適当な尿素、蔗糖、或はリンゴ酸等の有機酸を添加剤として添加することにより、大きな比表面積を得ている。

【0028】上記のようにして製造した触媒活性成分を、そのまま又は適当な粘結剤などの成形助剤と共にペレット状に押出または圧縮成形、或はハニカム状等に押出成形して使用しても良いが、適宜当業界周知の担体に担持させて使用しても良い。

【0029】本発明の分解触媒を用いて、排ガスにアンモニアや炭化水素等の還元剤を添加すること無しに、触媒と接触させて窒素酸化物を直接分解することができる。移動発生源や小型固定発生源からの排ガス中の窒素酸化物分解除去に還元剤が必要な還元触媒を適用するには限界があり、直接分解が本発明の大きな利点の一つである。

【0030】分解触媒と排ガスとの接触は、当業界に周

知の充填層式或いは棚段式等の固定床流通型反応器、または本発明の触媒が単位重量当たりの活性が高い利点を活用して流動床型反応器により行うことができる。また、排出源の種類や規模に応じて種々の実用的形態をとることができ、本発明はこれには限定されない。

【0031】分解触媒に排ガスを接触させる温度は、本発明の触媒の分解活性が高い500℃-900℃が好ましい。他の脱硝処理、例えば都市ゴミ焼却炉の排ガス処理が200℃以下、バナジウム・チタン系触媒による工場排ガス処理が300-400℃、ガソリンエンジンやガスタービンの排ガス処理が400-450℃で行われるのに対して、本発明の触媒による窒素酸化物の脱硝処理の作動温度は高温である点に特色があり、冷却手段等を用いて予め排ガス温度を下げる温度調整が不要である。

【0032】

【実施例】本発明を更に具体的に説明するため実施例を記載するが、本発明はこれにより限定されるものではない。なお、ここでガス組成を示す%は全て容量%であり、触媒及び原料、中間体の組成を示す%は全て重量%である。また触媒の分解活性は、NOのN₂への転化率で表し、数式1により計算する。

【0033】

【数式1】 分解率 = $2 [N_2]_{out} / [NO]_{in}$
ここで $[N_2]_{out}$ は反応器出口ガスのN₂濃度
 $[NO]_{in}$ は反応器入口ガスのNO濃度

【0034】【実施例1】

触媒の調製例1

Fe(NO₃)₃・6H₂O、Ti(NO₃)₄、及びSr(NO₃)₂・2H₂Oの各0.4M水溶液を当量比で0.4:0.6:1の割合で用意し、添加剤を加えて室温で混合した。これを350℃に加熱しつつ回転噴霧器*

$$W/F = \text{触媒重量 (g)} / \text{反応器流入ガス流速 (cm}^3/\text{sec)} \\ = [g] [sec] / [cm^3]$$

【0038】分解活性の評価2

本発明のSrTi_{0.8}Fe_{0.2}O₃触媒に上記評価1と同様にして、NOが1%、O₂が10%、Heが89%の混合ガス（即ち酸素共存下）を接触させて分解活性を調べ、結果を表1に示した。

【0039】前記した反応温度600、700、800℃における評価結果から、表1の通り本発明の分解触媒のNO転化率は、既知のペロブスカイト型触媒より顕著に高く、しかも分解温度800℃以上においても転化率90%以上に、活性が温度と共に増進する傾向が窺われる。また本発明の分解触媒は、酸素の存在下でも高い分解活性を有していることが判る。

【0040】【実施例2】

触媒の調製例3

硝酸第一鉄水溶液に代えてCo(NO₃)₂の0.4M水溶液を用いた他は上記調製例1と同様にして、本発明

*へ供給し、噴霧量を100cm³/分に調整したノズルから断熱的に120℃で空気流中へスプレーして、霧状態で350℃に保持した電気炉の中を落下させ、生成した粉体を炉の下部に設けたサイクロンで捕集して原料粉末を得た。この原料粉末を空气中で650℃で1時間仮焼し、次いで850℃で5時間焼成して触媒活性成分SrTi_{0.8}Fe_{0.2}O₃の粉末を得た。このもののX線結晶解析により、この触媒成分がペロブスカイト型結晶構造を持つことを確認した。この粉末を500kgf/cm²の圧縮力で等方圧成形し、得られたペレットを粉砕し分級して粒度が0.31mm-0.71mmの顆粒状の本発明の触媒SrTi_{0.8}Fe_{0.2}O₃を得た。比表面積はこの顆粒の液体窒素温度でのN₂吸着量からBET法により測定し、7.4m²/gであった。

【0035】触媒の調製例2

上記原料を用い、当量比を変えてTi/Fe比が0.2/0.8から0.8/0.2に該当する本発明の触媒を得た。

【0036】分解活性の評価1

内径10mmの円筒形充填層型反応器に上記触媒5.0gを充填し、反応器外壁を電熱加熱して触媒層の温度を所定に保ちながら、1%NO含有Heガス（即ち酸素非存在下）を接触時間W/F=3.0g・sec/cm³となる流量（即ち100cm³/分）で流し、出口ガスのN₂濃度をガスクロマトグラフ分析計により測定し、数式1によりNOからN₂への転化率として計算し、表1に示した。なおW/Fは触媒単位重量当たりの触媒活性を表示する接触時間の次元を持ち、数式2により計算される。

【0037】

【数式2】

の触媒SrTi_{0.8}Co_{0.2}O₃を得た。

【0041】触媒の調製例4

上記原料を用い、当量比を変えてTi/Co比が0.2/0.8から0.9/0.1に該当する本発明の触媒を得た。

【0042】分解活性の評価1

前記と同様に、1%NO含有Heガス（即ち酸素非存在）を用いて反応温度600、700、800℃における活性評価を行い、結果を表1に示した。本発明の分解触媒は既知のペロブスカイト型複合酸化物より高い活性を有し、しかも高温領域において活性がより大きいことが判る。

【0043】【実施例3】

触媒の調製例5

Fe(NO₃)₃・6H₂O、Zr(NO₃)₄・5H₂O、及びSr(NO₃)₂・2H₂Oの各0.4M

水溶液を用いた他は前記実施例1の調製例1と同様にして、本発明の触媒 $\text{SrZr}_{0.8}\text{Fe}_{0.2}\text{O}_3$ を得た。

【0044】分解活性の評価1

前記と同様に、1%NO含有Heガス（即ち酸素非存在）を用いて活性評価を行い、結果を表1に示した。本発明の分解触媒は既知のペロブスカイト型複合酸化物より活性が高く、且つ高温領域において活性がより大きいことが判る。

【0045】[実施例4]

触媒の調製例6

硝酸第一鉄水溶液に代えて $\text{Co}(\text{NO}_3)_2$ の0.4M水溶液を用いた他は上記調製例5と同様にして、本発明の触媒 $\text{SrZr}_{0.8}\text{Co}_{0.2}\text{O}_3$ を得た。

【0046】分解活性の評価1

前記と同様に、1%NO含有Heガス（即ち酸素非存在）を用いて活性評価を行い、結果を表1に示した。本発明の分解触媒は既知のペロブスカイト型複合酸化物より活性が高く、且つ高温領域において活性がより大きいことが判る。

【0047】[比較例1] 本発明の一般式 $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ の $x=1$ 、 $x=0$ に相当するペロブスカイト型複合酸化物 SrFeO_3 、 SrTiO_3 を夫々実施例1と同様にして調製し、実施例1と同様に活性評価を行い、結果を表1に示した。分解活性は本発明の分解触媒に遠く及ばないことが判る。

【0048】[比較例2] 本発明の一般式 SrTi_{1-x} *

* Co_xO_3 の $x=1$ に相当するペロブスカイト型複合酸化物 SrCoO_3 を実施例2と同様にして調製し、実施例2と同様に活性評価を行い、結果を表1に示した。分解活性は本発明の分解触媒に遥かに及ばないことが判る。

【0049】[比較例3] 本発明の一般式 $\text{SrZr}_{1-x}\text{M}_x\text{O}_3$ の $x=0$ に相当するペロブスカイト型複合酸化物 SrZrO_3 を実施例3と同様にして調製し、前記同様に活性評価を行い、結果を表1に示した。分解活性は本発明のNO分解触媒に及ばないことが判る。

【0050】[比較例4] La硝酸塩、Sr硝酸塩、及びCo硝酸塩の水溶液を用いた以外は実施例1と同様に製造して得られた比表面積 $4.9\text{ m}^2/\text{g}$ を有する既知のペロブスカイト型金属酸化物である $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ を用い、実施例1と同じ反応器を使用し、同じ条件で評価した結果を表1に記載した。上記比較例1の複合酸化物と比べてかなり活性が高いが、本発明の分解触媒と比較して 700°C 、 800°C における活性が6割程度であり、また温度を 800°C 以上に上げてても活性増加はあまり期待できないことを示しており、前記一般式中のBとMが共に必要なことが判る。また、酸素存在下における活性低下も本発明の分解触媒と比べて激しいことが判る。

【0051】

【表1】

排ガス中の酸素	酸素非存在 $\text{O}_2 = 0\%$		酸素共存 $\text{O}_2 = 10\%$	
	600	700	800	800
反応温度 $^\circ\text{C}$				
実施例1				
$\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_3$	5.1	11.1	14.6	
$\text{SrTi}_{0.6}\text{Fe}_{0.4}\text{O}_3$	11.8	40.8	67.9	
$\text{SrTi}_{0.4}\text{Fe}_{0.6}\text{O}_3$	13.8	51.4	79.1	46.1
$\text{SrTi}_{0.2}\text{Fe}_{0.8}\text{O}_3$	13.5	52.8	82.7	
実施例2				
$\text{SrTi}_{0.8}\text{Co}_{0.2}\text{O}_3$	5.5	15.2	25.9	
$\text{SrTi}_{0.6}\text{Co}_{0.4}\text{O}_3$	10.0	33.3	52.0	
$\text{SrTi}_{0.4}\text{Co}_{0.6}\text{O}_3$	13.8	51.4	79.1	
$\text{SrTi}_{0.2}\text{Co}_{0.8}\text{O}_3$	13.5	51.6	79.6	
実施例3				
$\text{SrZr}_{0.8}\text{Fe}_{0.2}\text{O}_3$	13.2	48.3	72.4	
実施例4				
$\text{SrZr}_{0.8}\text{Co}_{0.2}\text{O}_3$	10.1	30.1	45.6	
比較例1				
SrFeO_3	2.1	6.3	7.5	
SrTiO_3	2.7	10.6	22.9	
比較例2				

	(7)	特開平11-151440
11		12
SrCoO ₃	2.8 14.4 14.0	
比較例3		
SrZrO ₃	2.2 12.9 40.0	
比較例4		
La _{0.8} Sr _{0.2} CoO ₃	9.2 26.1 42.0	8.4

【0052】

【発明の効果】本発明の窒素酸化物分解触媒は、還元剤を使用せずにNOを高い分解率で直接N₂とO₂に分解することができるので、脱硝性能が排ガスの組成や燃焼器の種類に依存せず、幅広い適用が可能である。また、還元剤使用のランニングコストや還元剤供給制御装置等の装備が不要であり、経済的にも優れている。

【0053】本発明の窒素酸化物分解触媒は、酸素存在下でも活性の低下が比較的緩やかであり、排ガス中にかなりの酸素を含む空燃比の高いディーゼルエンジン等から排出されるNOの直接分解除去に適している *

*【0054】本発明の窒素酸化物分解触媒は、従来のNO_x分解触媒に比べ分解活性が発現する温度が600℃以上と高く、しかも或る温度範囲においては高温になるに伴い活性も高くなる傾向が強いので、高温排ガス中のNO_xの分解除去に適している。

【0055】本発明の分解触媒を用いる際は、従来の触媒のように冷却等の手段により排ガス温度を低下させる必要がないため、排ガス処理装置をコンパクトにでき、家庭用或は室内空気清浄化用途への適用可能性が大きい。

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